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Preliminary communication

PREPARATION AND CHARACTERISATION OF TRIS- μ -[BIS(DIPHENYLPHOSPHINO)METHANE] DIPLATINUM(0)

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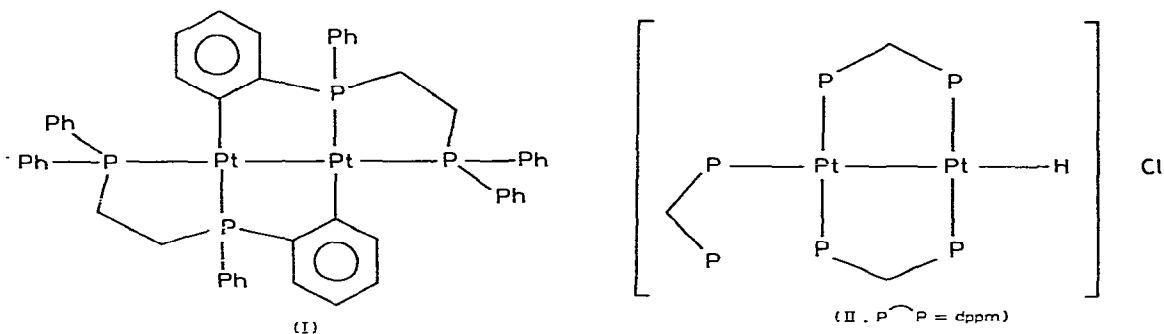
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Summary

The preparations of $[\text{Pt}_2(\text{dppm})_3]$ (dppm = bis(diphenylphosphino)methane) by three different routes are described, and a propellane-like structure is proposed for the complex on the basis of multinuclear NMR studies.

In 1978, Vaska and coworkers [1] reported some catalytic reactions of a complex described as $[\text{Pt}_2(\text{dppm})_3]$ (dppm = bis(diphenylphosphino)methane), although the method by which this complex was prepared was not mentioned, and no analytical, structural or spectroscopic data were reported. In view of his recent report that the compound originally described as a platinum(0) tetramer, $[\text{Pt}_4(\text{dppe})_4]$ (dppe = bis(diphenylphosphino)ethane) [2], is in reality a cyclometallated diplatinum(I) complex of structure I [3], it seemed timely to report our own observations upon the platinum(0)-dppm system.

It has been recognised for some years that the reduction of $[\text{Pt}(\text{dppe})_2]\text{Cl}_2$ or $[\text{Pt}(\text{tppme})\text{Cl}_2]$ in the presence of excess tppme (tppme = 1,1,1-tris(diphenylphosphinomethyl)ethane) with $\text{Na}[\text{BH}_4]$ in aqueous ethanol produces $\text{Pt}^0(\text{dppe})_2$ [4,5] or $[\text{Pt}^0(\text{tppme})_2]$ [6,7], respectively. These complexes form yellow crystals, and the crystal structure of the latter compound [7] unambiguously establishes its identity as a platinum(0) monomer: our own multinuclear NMR observations [8] upon $[\text{Pt}(\text{dppe})_2]$ and $[\text{Pt}(\text{tppme})_2]$ and $^{13}\text{C}_6\text{D}_6$ confirm that they retain their monomeric structure in solution. In



contrast, when $[\text{Pt}(\text{dppm})_2] \text{Cl}_2$, or $[\text{Pt}(\text{dppm})\text{Cl}_2]$ in the presence of one mole equivalent of dppm, are reduced by $\text{Na}[\text{BH}_4]$ in aqueous ethanol, only the diplatinum(I) hydride $[\text{Pt}_2 \text{H}(\text{dppm})(\mu\text{-dppm})_2] \text{Cl}$ (II) is obtained, in excellent yield [9–11]. However, we now find that if $[\text{Pt}(\text{dppm})\text{Cl}_2]$ in the presence of two mole equivalents of dppm (or $[\text{Pt}(\text{cod})\text{Cl}_2]$ (cod = 1,5-cyclooctadiene) in the presence of three mole equivalents of dppm) are treated with sodium tetrahydroborate in aqueous ethanol, an essentially quantitative yield of a red powder of empirical formula $[\text{Pt}_2(\text{dppm})_3]$ (Found: C, 57.8; H, 4.4; Cl < 0.06. $\text{C}_{75}\text{H}_{66}\text{P}_6\text{Pt}_2$ calcd.: C, 58.36, H, 4.31; Cl, 0.00%) is obtained. The same complex has also been isolated by treating $[\text{Pt}(\text{PPh}_3)_4]$ suspended in ethanol with two mole equivalents of dppm, or by the reduction of $[\text{Pt}_2 \text{Cl}_2(\mu\text{-dppm})_2]$ [12] with ethanolic $\text{K}[\text{OH}]$ in the presence of two mole equivalents of dppm. This complex has the same stoichiometry as the red

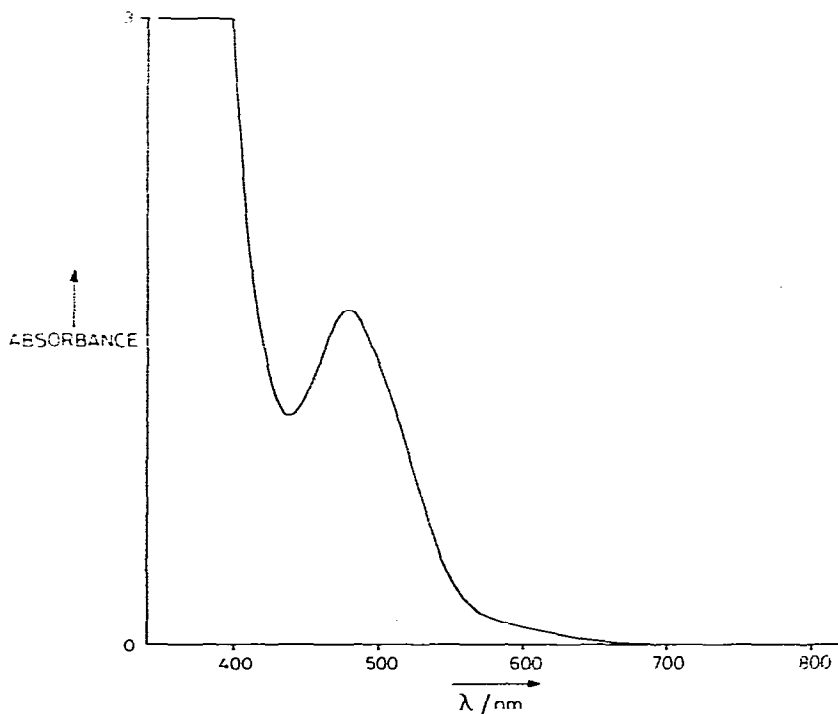
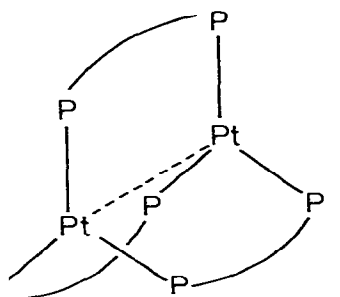


Fig. 1. Electronic spectrum of $[\text{Pt}_2(\text{dppm})_3]$ in benzene.



(III, P—P = dppm)

platinum analogue $[\text{Pd}_2(\text{dppm})_3]$ [13–16], the preparation and reactivity of which are well documented, but of which no spectroscopic characterisation or structural assignment has been reported.

Like the palladium analogue, $[\text{Pt}_2(\text{dppm})_3]$ dissolves in benzene to produce a deep red solution. The colour is due to the presence of a band in the electronic spectrum (see Fig. 1) at 479 nm, a feature absent in the electronic spectrum of $[\text{Pt}(\text{PPh}_3)_4]$ and $[\text{Pt}(\text{dppe})_2]$ in the same solvent, and indicative of the presence of significant Pt—Pt interaction. The ^1H NMR spectrum of $[\text{Pt}_2(\text{dppm})_3]$ in C_6D_6 reveals that all six of the methylene protons of the dppm ligands are equivalent forming a pentuplet pattern (ca. 1/8/18/8/1) with δ 3.18 ppm characteristic of three magnetically equivalent ligands, bridging between two platinum atoms, with $^3J(\text{PtH})$ 30.9 Hz. The simplest structure compatible with this data is the propellane-like structure illustrated in III, and this postulate is strongly supported by the ^{195}Pt NMR spectrum in C_6D_6 which is illustrated in Fig. 2. The gross structure of a quartet of quartets is anticipated from the principal ^{195}Pt NMR active isotopomer (cf. [12]), and reveals $^1J(\text{PtP})$ 4456 Hz and $^2J(\text{PtP})$ 51 Hz, and the weaker satellites are due to the isotopomer containing two ^{195}Pt atoms. Final confirmation of III as the structure of $[\text{Pt}_2(\text{dppm})_3]$ in solution comes from the ^{31}P NMR spectrum, which shows all the phosphorus atoms to be chemically equivalent, and shows a complex splitting pattern which may be understood in terms of an $\text{AA}'\text{A}''\text{A}''' \text{A}''''\text{A}''''' \text{X}$ spin system superimposed on an $\text{AA}'\text{A}''\text{A}''' \text{A}''''\text{A}''''' \text{XX}'$

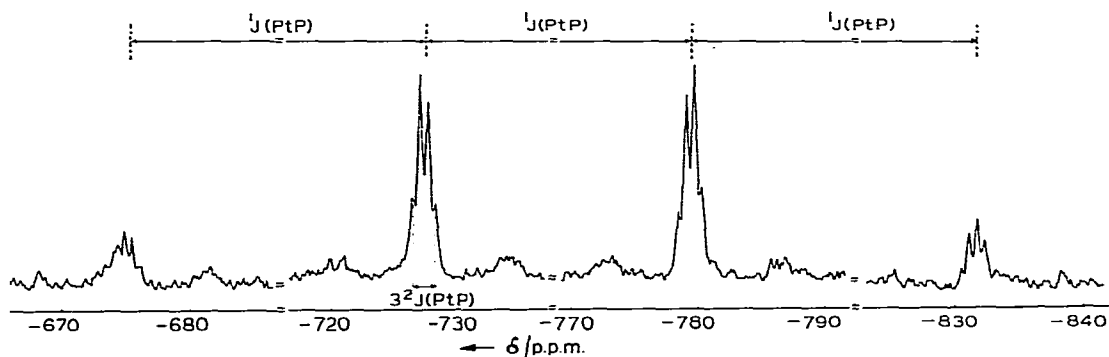


Fig. 2. ^{195}Pt $\{^1\text{H}\}$ NMR spectrum (89.56 MHz) of $[\text{Pt}_2(\text{dppm})_3]$ in C_6D_6 . (Positive ppm values are to high frequency of the reference compound $[\text{Pt}(\text{dppm})\text{Cl}_2]$).

spin system. It is not possible to confirm whether or not this is the same complex as that reported by Vaska, in the absence of any reported details of his synthetic methods or spectroscopic properties of his complex. However, in the absence of evidence to the contrary, it is probable that the complexes are the same.

The complex $[\text{Pt}_2(\text{dppm})_3]$ (III) is extremely reactive yielding isolable products with CO , SO_2 , S_8 , O_2 , CH_3I , $\text{C}_2\text{H}_5\text{I}$, CH_2Cl_2 , CH_2I_2 , C_2H_2 , $\text{Au}(\text{PPh}_3)\text{Cl}$, Ph_3SnCl , Bu_3SnCl , SnCl_4 , HgCl_2 and a wide range of transition metal carbonyl derivatives, and details of these reactions will be published elsewhere. It is, however, apposite to report here the product of the protonation reactions of $[\text{Pt}_2(\text{dppm})_3]$. Earlier [11], we reported our failure to deprotonate II in an attempt to prepare III, and speculated as to whether protonation of III would yield II. We now find that a benzene solution of III reacts with an aqueous buffer solution ($\text{pH} = 6.88$) to yield upon addition of $\text{K}[\text{PF}_6]$ the complex $[\text{Pt}_2\text{H}(\text{dppm})(\mu\text{-dppm})_2][\text{PF}_6]$ in excellent yield (90%), which highlights the reactivity of III, and particularly its strong basic character.

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